Atmospheric Chemistry Experiment (ACE) measurements of elevated Southern Hemisphere upper tropospheric CO, C_2H_6, HCN, and C_2H_2 mixing ratios from biomass burning emissions and long-range transport

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[1] Infrared Fourier transform spectra recorded at 0.02 cm^{-1} resolution by the Atmospheric Chemistry Experiment (ACE) show elevated levels of the relatively long-lived biomass burning products CO, C_2H_6, HCN, and C_2H_2 in the upper troposphere and lower stratosphere at $15°S-45°S$ latitude from 30 September to 3 November 2004. Mixing ratios up to 260 ppbv (10^{-9} per unit volume) for CO, 1470 pptv (10^{-12} per unit volume) for HCN, and 1.67 ppbv for C_2H_6 are observed in the upper troposphere and their variations are highly correlated reflecting their similar lifetimes and emission origin. Back trajectory calculations and maps of fire distributions for the time period indicate the elevated levels likely originated from regions of tropical fire emissions in South America or Africa with cases identified with elevated emissions reaching close to the lower stratosphere. **Citation:** Rinsland, C. P., G. Dufour, C. D. Boone, P. F. Bernath, and L. Chiou (2005), Atmospheric Chemistry Experiment (ACE) measurements of elevated Southern Hemisphere upper tropospheric CO, C_2H_6, HCN, and C_2H_2 mixing ratios from biomass burning emissions and long-range transport, *Geophys. Res. Lett.*, *32*, L20803, doi:10.1029/2005GL024214.

1. Introduction

[2] Biomass burning is a major source of carbon dioxide (CO_2), methane (CH_4), nitrogen oxides (NO_x), and particulate emissions on a global scale [*Crutzen et al.*, 1979; *Crutzen and Andreae*, 1990]. Reactions with the hydroxyl radical (OH), the dominant oxidizing chemical in the atmosphere, drive atmospheric oxidation through reaction with chemicals emitted from the Earth's surface, thus creating new chemicals that are more easily scavenged and removed by aerosols, clouds and rain. Many of these molecules including methane lead to the chemical production of tropospheric ozone. Biomass burning is a significant source of greenhouse gases, leading to the production of chemically-active trace gases important in determining air quality. Biomass burning may be a significant driver for climate change.

[3] Agricultural practices result in annual maximum emissions from fires in tropical savannah regions of Africa and South America during August to October [*Fishman et al.*, 1991; *Browell et al.*, 1996; *Watson et al.*, 1990]. Pollution from those regions during this season has been reported from several studies with a variety of sensing techniques including aircraft *in situ* sampling and differential absorption lidar (DIAL) measurements over the northwestern Pacific during the Pacific Exploratory Mission in the Tropical Pacific Phase A (PEM-Tropics A) from August to September 1966 [*Hoell et al.*, 1999], ground-based infrared remote sensing [*Rinsland et al.*, 1998, 2001], and satellite-based techniques [*Connors et al.*, 1999; *Fishman et al.*, 1991; *Bremer et al.*, 2004; *Luo et al.*, 2004]. The purpose of the present study is to report and interpret upper tropospheric mixing ratios of the long-lived biomass emission products CO, C_2H_6, and HCN derived from high spectral resolution infrared solar occultation measurements at southern hemisphere lower to mid-latitudes by the Atmospheric Chemistry Experiment (ACE) instrument from 30 September to 3 November 2004. The relatively long lifetimes of CO [*Logan et al.*, 1981], HCN [*Li et al.*, 2000; *Singh et al.*, 2003], and C_2H_6 [*Hough*, 1991] make them important indicators of how transport redistributes pollutants on a global scale. ACE observations show upper tropospheric CO volume mixing ratios as high as 260 ppbv (1 ppbv = 10^{-9} per volume), HCN mixing ratios up to 1470 pptv (1 pptv = 10^{-12} per volume), and a maximum C_2H_6 mixing ratio of 1.67 ppbv. Elevated C_2H_2 mixing ratios have also been detected in plumes. Back trajectory calculations for measurements with the highest mixing ratios indicate the emissions likely originated near the surface from tropical regions of intense fire emissions over tropical South America or Africa. The results are presented and compared with previously reported southern hemisphere dry season measurements.

2. Measurements

[4] The ACE experiment, also known as SCISAT-1, was launched on 12 August 2003 into a 74° inclined orbit by a U.S.-supplied Pegasus XL at 650 km altitude [*Bernath et*

al., 2005]. The small Canadian-designed and built satellite contains three instruments with a shared field of view, and with the primary goal of recording high resolution atmospheric spectra taking advantage of the high precision of the solar occultation technique. An infrared Fourier transform spectrometer (FTS) records solar spectra below altitudes of 150 km at a spectral resolution of 0.02 cm^{-1} (maximum optical path difference of ±25 cm) from 750 to 4400 cm^{-1}. The instrument is self-calibrating as low Sun solar occultation spectra are divided by exoatmospheric solar spectra from the same occultation. The ACE orbit yields tropical to high latitude occultations in both hemispheres with a vertical resolution of $3-4$ km. Frequent Arctic occultation events are recorded during the winter and early spring period of maximum ozone depletion. Additional instruments onboard SCISAT-1 are the MAESTRO (Measurement of Aerosol Extinction in the Stratosphere and Troposphere by Occultation), a two channel UV-visible spectrophotometer, and two imagers with optical filters at 0.525 and 1.02 μm.

[5] While the primary focus is quantifying ozone loss in the stratosphere, the high-quality observations of the mesosphere and lower thermosphere as well as the free troposphere are also obtained. Orbital coverage yields opportunities to study pollution events in the middle and upper troposphere, and we focus here on the molecules CO, C_2H_6, HCN, and C_2H_2 from southern hemisphere lower-midlatitudes ($15°S-45°S$) recorded with the ACE FTS between September 30 and November 3, 2004.

3. Analysis

[6] Routine ACE FTS science measurements began in February 2004, and we describe results from observations during September to early November 2004 at midlatitudes of the southern hemisphere. We rely on version 2.2 retrievals [*Boone et al.*, 2005], which provide volume mixing ratios with statistical uncertainties from an algorithm that retrieves profiles of temperature and the volume mixing ratios of individual molecules from fits to multiple species in pre-selected microwindows over pre-specified altitude ranges. Temperature profiles are retrieved from the occultation spectra assuming a realistic CO_2 volume mixing ratio profile. Profile retrievals below 12 km altitude assume temperatures derived by the Canadian Meteorological Centre (CMC) for the location of the observation. Spectroscopic parameters and absorption cross sections are based on HITRAN 2004 [*Rothman et al.*, 2005]. Microwindows for CO retrievals were selected in the $4209-4277$ cm^{-1} region with CH_4 lines the primary interference. Retrievals for HCN used windows from $3277-3358$ cm^{-1}, and C_2H_6 retrievals relied on a single microwindow at $2976-2977$ cm^{-1} [*Rinsland et al.*, 1998]. Systematic errors include uncertainties in the ACE retrieval algorithm, retrieved temperatures, and errors in the tangent heights for individual spectra, and errors in the HITRAN 2004 spectroscopic parameters [*Rothman et al.*, 2005]. Systematic differences in mixing ratios due to differences in the retrieval algorithm are estimated to be 5% or less based on comparisons of ACE profiles retrieved in the upper troposphere with profiles retrieved for the same events assuming ACE-derived temperatures and tangent heights
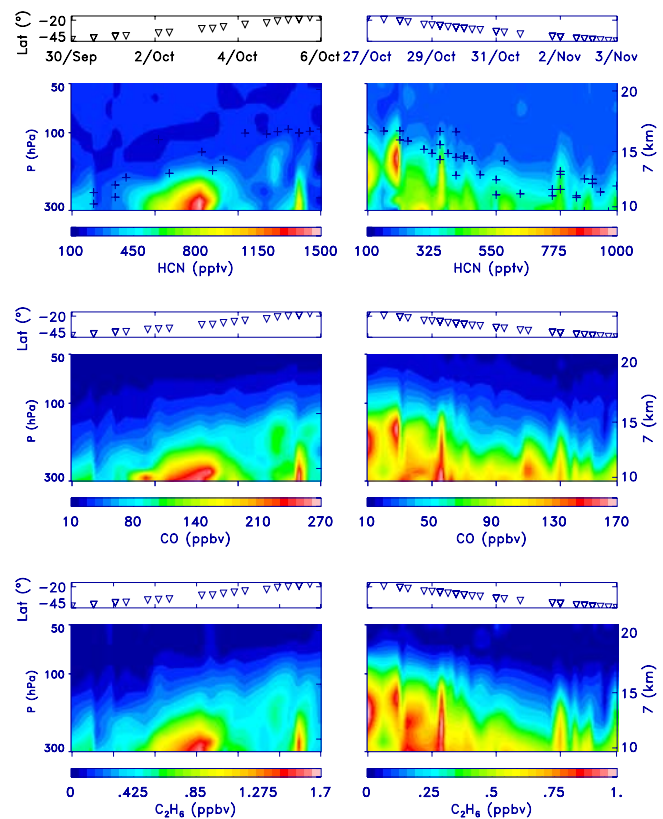

Figure 1. Time series of ACE version 2.2 measurements of CO, HCN, and C_2H_6 recorded at southern hemisphere midlatitudes during sunsets and sunrises between September 30 and November 3, 2004. The latitude coverage for each observation is shown above contours of sunset or sunrise measurements as a function of pressure. Approximate altitudes are indicated on the right vertical axis. Plus symbols in the top panels show tropopause heights from NCEP for the measurement locations.

with results from an algorithm developed at the NASA Langley Research Center [*Rinsland et al.*, 2005].

[7] As the ACE orbit is optimized for high latitude occultation coverage, measurements at middle and low latitudes are recorded only over limited time spans with latitudinal coverage that changes rapidly with time. Measurements are obtained at a moderate beta angle (the angle between the orbital plane and the Earth-Sun vector). Southern hemisphere mid-latitude coverage began with sunsets near 45°S latitude on 30 September 2004 with latitudes decreasing to 15°S on 6 October 2004 with the beta angle increasing from 40.5° to 53.8°. Sunrises were recorded at 15°S to 45°S from 26 October to 3 November 2004 with a beta angle 48.2° at the start of the time period decreasing to 29.0° at the end. We focus on CO, HCN, C_2H_6, C_2H_2 tropospheric measurements during these two time periods when biomass burning south of the equator is most intense [*Hao and Liu*, 1994].

[8] Figure 1 displays ACE version 2.2 tropospheric and lower stratospheric CO, HCN, and C_2H_6 volume mixing ratio measurements recorded during southern hemisphere sunrises or sunsets. The latitude of the individual measurements is indicated at top. Noisy measurements have been excluded based on the statistical uncertainties. Tropopause

heights from NCEP (National Center for Environmental Prediction) measurements for the measurement locations are displayed with plus symbols in the upper panel. Maximum volume mixing ratios of 260 ppbv for CO, 1470 pptv for HCN, and 1.67 ppbv for C_2H_6 were measured between 3 and 5 October at 262 hPa, (~10.5 km), 298 hPa (~9.5 km), and at 298 hPa (~9.5 km), respectively. The right panel displays ACE version 2.2 upper tropospheric CO, HCN, and C_2H_6 mixing ratio measurements from sunrises between 26 October and 3 November 2004. Highest CO and HCN mixing ratios were measured in the upper troposphere on 27–29 October 2004. The CO volume mixing ratio peak of 168 ppbv was measured at 262 hPa (~10.5 km) during sunrise 6532 and the maximum HCN volume mixing ratio of 988 pptv was measured during sunrise 6512 at 140 hPa (~14.5 km). A maximum C_2H_6 mixing ratio of 1.10 ppbv was measured at 191 hPa (~12.5 km) from sr6532 (sunrise 6532) during this time period. The elevated mixing ratios of the October 29 plume reached close to the tropopause.

4. Discussion

[9] Biomass burning plumes in the free troposphere are clearly visible through strong enhancements of CO, HCN, and C_2H_6 mixing ratios in ACE FTS measurements (Figure 1). The increases in each of these species are well correlated. This is also illustrated by the correlation plot presented in the upper panel of Figure 2 for HCN and CO derived by combining the sunrise and sunset measurements from the 30 September to 3 November time period. A correlation coefficient of 0.90 is derived from the 56 occultations recorded over that time period. Regarding the individual profiles, the correlation of these different biomass burning products is also excellent, especially at the peak. An example of individual profiles of CO, HCN and C_2H_6 is given on the left panel of the lower plot in Figure 2. The peaks of the profiles are situated at 8.5 km for this occultation (sunset 6139). For comparison, the right panel of the lower plot of Figure 2 displays the profiles of CO, HCN, and C_2H_6 for the occultation ss6124 that does not show any enhancement typical of biomass burning plumes. It is important to point out that the ACE FTS can also measure C_2H_2 by using microwindows from 3268–3305 cm^{-1}, but these retrievals are often compromised by ice contamination on the detectors [Boone et al., 2005] so we display values for only examples. The C_2H_2 profile for occultation ss6139 is also peaked at 8.5 km with mixing ratio of 320 pptv (C_2H_2 mixing ratios in the free troposphere are typically below 100 pptv). The uncertainties displayed in the lower panel of Figure 2 correspond only to the statistical errors resulting from the fitting procedure.

[10] The ratio of C_2H_2/CO is an indicator of the relative age of the air mass and the degree of atmospheric processing [Smyth et al., 1996, 1999] and was measured over the central and South Pacific during the PEM-Tropics A field mission [Talbot et al., 1999]. Air masses with this ratio less than 1 correspond to photochemically aged and well mixed air parcels. ACE measurements between 15°S and 45°S (those displayed in Figures 1 and 2) for upper tropospheric altitudes yield a ratio of (0.9509 ± 0.4446) pptv/ppbv for the mean and standard deviation based on a criterion that removes poor measurements with an uncertainty/value >1.0. The value is
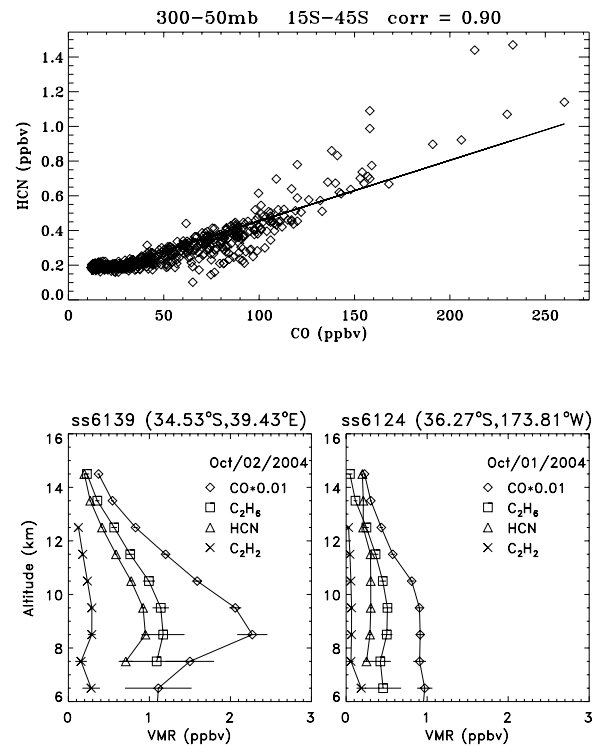

Figure 2. Upper panel: correlation between the volume mixing ratios of CO and HCN derived from the ACE version 2.2 measurements from measurements between 30 September and 3 November, 2004 and the correlation coefficient. Lower panel: ACE free tropospheric profiles and their uncertainties versus altitude with an example of elevated CO, C_2H_6, HCN, and C_2H_2 volume mixing ratio (VMR) profiles (left panel) compared with profiles from a background case (right panel). Locations and run numbers of the two sunset (ss) occultations are displayed.

within the range of 0.2–2.2 pptv/ppbv reported from PEM-Tropics A measurements [Talbot et al., 1999], indicating ACE measurements sampled primarily aged air masses. However, if only occultations with enhanced CO, HCN, and C_2H_6 are considered, the mean value of the C_2H_2/CO ratio is about 1.2. This does not mean necessarily that these air masses are younger. They can be quite photochemically aged but the mixing with background air may be incomplete [Talbot et al., 1999]. Looking at the secondary species typical of biomass burning could be a way to estimate the age of the plumes. However, back trajectory calculations also give us the age of the plumes as well as the likely source area and the role of the long-range chemical transport.

[11] Kinematic back trajectory calculations were performed with the HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated Trajectory) model [Draxler and Rolph, 2003]. Backward trajectories over 7 days for the occultation ss6139 (Figure 2) at the altitude of the peak (8.5 km) and at the altitudes below (7.5 km) and above (9.5 km) the peak indicate air masses sounded at these altitudes during this occultation come from lower altitudes (~4 km) above Brazil, in agreement with long-range transport already observed in biomass burning plumes [Pack et al., 2003]. Furthermore, MODIS (Moderate Resolution Imaging

Spectroradiometer [*Giglio et al.*, 2003]) maps over Brazil for the corresponding days (around 7 days before the measurements) show fire counts all around the area from where the air masses originated. Back trajectories were also run for the 2 occultations showing the most important enhancements during the two time periods studied. Calculations were performed for altitudes between 8 and 11 km. The back trajectories suggest that all of our observed enhancements in HCN, CO, and C_2H_6 likely originated from emissions at lower altitudes and latitudes from regions of Brazil and South America, where frequent intense burning occurs during that time of the year. The ACE measurements are consistent with southern hemisphere CO, C_2H_6, and HCN columns retrieved from high spectral resolution infrared ground-based solar spectra, which show the pollution extends to midlatitudes of the southern hemisphere [*Rinsland et al.*, 1998, 2001].

5.　Summary and Conclusions

[12]　Solar occultation measurements recorded by the ACE Fourier transform spectrometer show elevated free tropospheric mixing ratios of CO, HCN, C_2H_6, and C_2H_2 at latitudes between $15°$ and $45°S$ from 30 September to 3 November 2004. Maps of fire locations, back trajectory calculations for ACE measurement locations, and previous studies suggest that the elevated mixing ratios originated from tropical fire emissions, most likely regions of tropical South America or Africa. Mixing ratios of CO up to 260 ppbv, 1470 pptv for HCN, and 1.67 ppbv for C_2H_6 have been measured in the upper free troposphere. High correlations between the mixing ratios of the 3 molecules are consistent with a common origin for the emissions and their similar lifetimes with cases of elevated mixing ratios extending to near the tropopause identified near the end of the time period. Despite the limitation that retrievals are often compromised by ice contamination on the ACE detectors, elevated C_2H_2 mixing ratios have also been detected in plumes. Although measurements of CO, C_2H_6, and HCN are routinely measured from stations of the Network for the Detection of Stratospheric Change (NDSC) (http://www.ndsc.ncep.noaa.gov), and CO is measured with a wide variety of techniques over an extended range of altitudes, but except for ACE, global satellite measurements of HCN are currently limited to determination of weekly zonal means between 0.06 and 30 hPa (24–70 km) by the Microwave Limb Sounder (MLS) on Aura [*Pumphrey et al.*, 2004].

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